FINAL REPORT

Investigation of hyperfine structure of various materials using all-electron full-potential program

AOARD 074044

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01 September 2008

Report Documentation Page

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
05 SEP 2008	**FInal**	**16-04-2007 to 15-05-2008**

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Investigation of hyperfine structure of various materials using all-electron full-potential program	**FA48690714044**
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)	5d. PROJECT NUMBER
Kanichi Nakagawara	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT NUMBER
Nihon Gene Research Laboratories Inc.,2-11-3, Ideka, Miyagino-ku,Sendai-shi 983-0012,Japan,JP,9830012	**N/A**

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
AOARD, UNIT 45002, APO, AP, 96337-5002	**AOARD**
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)
	AOARD-074044

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT
A specific example of first-principles hyperfine parameters is presented. Within density functional theory, the magnetic hyperfine properties are studied for a model molecule representing the heme moiety of nitrosylmyoglobin using so called all‐electron mixed basis method. The isotropic hyperfine parameters are calculated for the N atoms of nitric oxide agent and proximal histidine group by considering various values for Fe‐N(NO) bond distance and Fe‐N‐O angle. The values are compared with the available experimental data from EPR and ENDOR techniques in order to predict the most stable structure of nitrosylmyoglobin at low temperatures.

15. SUBJECT TERMS
Modelling & Simulation, Materials Science

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE	**Same as Report (SAR)**	**5**	
unclassified	**unclassified**	**unclassified**			

First-principles calculations of hyperfine parameters for nitrosylmyoglobin

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Within density functional theory, the magnetic hyperfine properties are studied for a model molecule representing the heme moiety of nitrosylmyoglobin using so called all-electron mixed basis method. The isotropic hyperfine parameters are calculated for the N atoms of nitric oxide agent and proximal histidine group by considering various values for Fe-N(NO) bond distance and Fe-N-O angle. The values are compared with the available experimental data from EPR and ENDOR techniques in order to predict the most stable structure of nitrosylmyoglobin at low temperatures.

Myoglobin is a heme-protein whose physiological importance is principally related to its ability to bind molecular oxygen. Myoglobin is a monomeric heme protein found mainly in muscle tissue where it serves as an intracellular storage site for oxygen. During periods of oxygen deprivation oxymyoglobin releases its bound oxygen, which is then used for metabolic purposes [1].

Each myoglobin molecule contains one heme prosthetic group inserted into a hydrophobic cleft in the protein (see Figure 1). Each heme residue contains one central coordinately bound iron atom that is normally in the Fe^{2+}, or ferrous, oxidation state. The oxygen carried by heme-proteins is bound directly to the ferrous iron atom of the heme prosthetic group. Oxidation of the iron to the Fe^{3+}, ferric, oxidation state renders the molecule incapable of normal oxygen binding. Hydrophobic interactions between the tetrapyrrole ring and hydrophobic amino acid R groups on the interior of the cleft in the protein strongly stabilize the heme
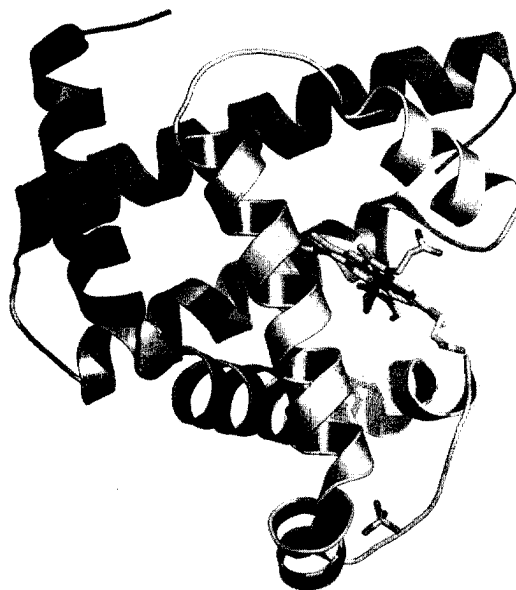

Figure 1. Model of helical domains in myoglobin.

protein conjugate. In addition a nitrogen atom from a histidine R group located above the plane of the heme ring is coordinated with the iron atom further stabilizing the interaction between the heme and the protein [2], as shown in Figure 2. In oxymyoglobin the remaining bonding site on the iron atom (the 6th

coordinate position) is occupied by the oxygen, whose binding is stabilized by a second histidine residue.

Various forms of myoglobin, may play a significant role in processes either promoting or protecting against oxidative stress [3 and 4]. Under conditions of myocardial damage or reperfusion of ischaemic heart tissue, the production of nitric oxide will increase, resulting in the formation of so-called nitrosylmyoglobin [5], which is a myoglobin with a NO attached to its Fe atom (see Figure 2). Nitric oxide bound to myoglobin results in a steady-state concentration of free nitric oxide and the level of nitric oxide has been found to regulate both oxygen uptake and H_2O_2 release in the heart tissues [6]. Also, Macrophages are thought to produce NO as a protective agent against invasive parasites [7].

Due to the facts described above, so far there have been many experimental and theoretical efforts in order to understand the mechanism of NO interaction with heme part of myoglobin protein. As both nitrosylmyoglobin and myoglobin itself are magnetically para-type, many experiments, using electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR) techniques, have been carried out in order to understand the magnetic and

Figure 2. Model for nitrosylmyoglobin.

hyperfine properties of this molecule [8-12]. However, as shown in Table 1, different groups have reported inconsistently different hyperfine values for N^γ, the N of NO agent. This is due to the fact that, there seems to be a structural transition at low temperatures in which the N^γ-Fe-N^ϵ axis, approximately perpendicular to the heme plane at room temperature, is tilted with respect to that plane when the temperature is lowered. A decrease in O-N^γ-Fe has been also suggested to occur at low temperatures [8]. Such changes can consequently affect the observed hyperfine spectra.

The above facts clarify the necessity of having reliable theoretical results as a reference to analyze the available experimental data. In this regard, within the context of density functional theory, we have performed a set of electronic structure calculations for nitrosylmyoglobin molecule
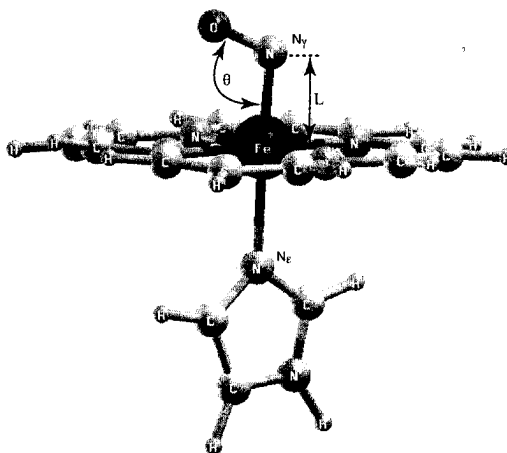
Table 1. Experimental values of isotropic hyperfine parameter Aiso (in MHz) for N and N in nitrosylmyoglobin.

Technique	Temperature (K)	Aiso		Reference
		$^{15}N_\gamma$	$^{14}N_\epsilon$	
EPR	77	±67	-	8
EPR	300	±53	-	9
ENDOR	5	±36.7	±17.5	10
ENDOR	10	-	±17	11

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to examine the effect of changes in N^γ-Fe bond length L and O-N^γ-Fe angle on the hyperfine properties of N^γ. Our calculations are based on local spin density approximation (LSDA) using so-called all-electron mixed-basis (AEMB) method [13].

In our calculations we consider a relatively large cubic supercell with a side of 16 Å. The integrations in reciprocal space are carried out using Γ point only. For the sake of simplicity, the heme part of myoglobin is modeled by a hydrogen-terminated molecule, as depicted in Figure 2. We adopted the coordinates reported from an X-ray diffraction for the myoglobin protein [14]. As regards the nitric oxide part of nitrosylmyoglobin structure, we have performed various electronic structure calculations with different L and α values. The isotropic hyperfine parameter A_{iso} is then calculated for $^{15}N^\gamma$, $^{14}N^\varepsilon$ and ^{57}Fe of each configuration.

Table 2 summarizes the calculated results for total energy, A_{iso} and the energy difference between the highest occupied molecular orbital, and the lowest unoccupied molecular orbital, defined as HOMO-LUMO gap, for each configuration S. A comparison between Table 1 and Table 2 shows that, the A_{iso} values obtained for N^γ and N^ε in configurations 5, S5, agree well with the corresponding experimental ENDOR data observed at 5 K. Interestingly, the S5

Table 2. Comparison of total energy, HOMO-LUMO gap (in ev) and isotropic hyperfine parameter (in MHz) obtained for nitrosylmyoglobin with different geometrical parameters L and θ, the Fe-

Structure	L	θ	Total energy	HOMO-LUMO	Isotropic Hyperfine parameter		
S					$^{15}N_\gamma$	$^{14}N_\varepsilon$	^{57}Fe
1	1.74	112	-62212.87	0.024	-21.36	5.56	5.98
2	1.74	120	-62213.01	0.006	-40.83	8.37	8.81
3	1.74	130	-62210.35	0.009	3.19	47.20	12.14
4	1.74	140	-62212.97	0.004	-90.87	18.64	14.42
5	1.74	150	-62213.36	0.109	35.37	-14.66	13.14
6	1.80	112	-62211.43	0.020	10.40	-4.43	5.12
7	1.80	120	-62210.48	0.008	2.52	2.12	8.03
8	1.80	130	-62210.37	0.010	-57.78	3.45	11.77
9	1.80	140	-62210.26	0.002	3.269	4.18	14.41
10	1.80	150	-62212.82	0.027	-101.78	22.91	15.38
11	1.89	112	-62210.35	0.019	-14.69	1.97	4.15
12	1.89	120	-62213.04	0.014	-27.42	7.03	7.1052
13	1.89	130	-62213.01	0.011	-46.98	11.47	10.79
14	1.89	140	-62212.98	0.232	-41.69	9.59	8.84
15	1.89	150	-62212.70	0.016	-86.91	21.16	15.36

has the lowest total energy value among the other configurations. In other words, it is probably the most stable structure of nitrosylmyoglobin at temperatures near 0 K.

While the experiment is unable to specify the sign of A_{iso} for $^{15}N^{\gamma}$ and $^{14}N^{\epsilon}$, our calculations show that they should have opposite signs. On the other hand, we know that the nuclear gyromagnetic factors of $^{15}N^{\gamma}$ and $^{14}N^{\epsilon}$ are -0.566 and 0.404, respectively. Accordingly, one can conclude that the sign of the spin density at $^{15}N^{\gamma}$ and $^{14}N^{\epsilon}$ nuclei should be the same. The respective A_{iso} values of 35.37 MHz and -14.16 MHz indicate that the spin density is more localized at the vicinity of $^{15}N^{\gamma}$ nucleus than at the vicinity of $^{14}N^{\epsilon}$ nucleus. In Other word, the NO agent seems to be more substantially spin-polarized than the proximal histidine group.

In conclusion, our calculations for nitrosylmyoglobin revealed that the isotropic hyperfine parameter of $^{15}N^{\gamma}$ is extremely sensitive to the Fe-$^{15}N^{\gamma}$-O angle and to the Fe-$^{15}N^{\gamma}$bond distance. Based on our calculations, the respective values of 1.74 Å and 150 were predicted for L and α. The spin polarization turned out to be more substantial on $^{15}N^{\gamma}$ than that on $^{14}N^{\epsilon}$.

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